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Structural properties of *trans*-cyclohexane-1,2-diamine complexes of copper(II) and zinc(II) acesulfamates

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The title compounds, trans-bis(trans-cyclohexane-1,2-diamine)bis(6-methyl-2,2,4-trioxo-3,4-dihydro-1,2,3-oxathiazin-3-ido)copper(II), $[Cu(C_4H_4NO_4S)_2(C_6H_{14}N_2)_2]$, (I), and *trans*-diaquabis(cyclohexane-1,2-diamine)zinc(II) 6-methyl-2,2,4-trioxo-3,4dihydro-1,2,3-oxathiazin-3-ide dihydrate, $[Zn(C_6H_{14}N_2)_2 (H_2O)_2](C_4H_4NO_4S)_2 \cdot 2H_2O_2$ (II), are two-dimensional hydrogen-bonded supramolecular complexes. In (I), the Cu^{II} ion resides on a centre of symmetry in a neutral complex, in a tetragonally distorted octahedral coordination environment comprising four amine N atoms from cyclohexane-1,2-diamine ligands and two N atoms of two acesulfamate ligands. Intermolecular $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds produce $R_2^2(12)$ motif rings which lead to two-dimensional polymeric networks. In contrast, the Zn^{II} ion in (II) resides on a centre of symmetry in a complex dication with a less distorted octahedral coordination environment comprising four amine N atoms from cyclohexane-1,2-diamine ligands and two O atoms from aqua ligands. In (II), an extensive twodimensional network of $N-H\cdots O$, $O-H\cdots O$ and $C-H\cdots O$ hydrogen bonds includes $R_2^1(6)$ and $R_4^4(16)$ motif rings.

Comment

Acesulfame (acs) is an oxathiazinone dioxide, systematically named 6-methyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide. It was discovered by Clauss (Clauss & Jensen, 1973) in 1967 and since 1988, after FDA (United States Food and Drug Administration) approval (Mukherjee & Chakrabarti, 1997), has been widely used as an artificial sweetener (Duffy & Anderson, 1998). Cyclohexane-1,2-diamine exists in two isomeric forms, *viz. cis* and *trans*. The *trans* isomer is more stable than the *cis* and probably because of this it has been well studied (Morooka *et al.*, 1991; Xu & Khokhar, 1992; Khokhar *et al.*, 1993). Recently, investigations of the chromotropic properties of its transition metal complexes have attracted much attention owing to the potentially versatile applications of these complexes such as temperature sensors. thermochromic pigments, temperature indicators, security and novelty printing, coatings, as well as in thermography and for recording optical information (Bamfield, 2002). The thermochromic phenomena observed in the transition metal complexes are generally associated with changes in the coordination geometry, ligand field strength and deaguation by heating. Previous studies have reported that similar cyclic diamine complexes exhibit colour changes and phase transitions as a result of hydrogen-bond breaking and reforming (El-Ayaan et al., 2001; Kapustyanyk & Korchak, 2000), liberation of neutral ligands (cyclohexane-1,2-diamine or aqua) from the structure of the complex (Pariya, Liao et al., 1998; İçbudak, Uyanık et al., 2007; İçbudak, Heren et al., 2005) and geometry changing from trans to cis isomers (Takahashi et al., 2002; Koner et al., 2002).

The hydrogen bonds existing in the structures also play an important role in the thermochromic phenomena, with changes in the absorption spectra (Das *et al.*, 1998; Koner *et al.*, 2002; Linert *et al.*, 2001; Pariya, Liao *et al.*, 1998). The chromotropic properties of acesulfame-amine-metal complexes have been studied extensively in this laboratory (İçbudak, Heren *et al.*, 2005; İçbudak *et al.*, 2006; İçbudak, Adıyaman *et al.*, 2007; İçbudak, Uyanık *et al.*, 2007). We report here the structures of *trans*-bis(acesulfamato)bis(*trans*-cyclohexane-1,2-diamine)copper(II), (I), and *trans*-diaquabis(cyclohexane-1,2-diamine)zinc(II) acesulfamate dihydrate, (II), in which hydrogen bonding leads to different two-dimensional supra-molecular networks.



The molecular structure of (I) and the atom-labelling scheme are shown in Fig. 1. The local structure around the Cu^{II} ion, which resides on a centre of symmetry, is that of a tetragonally distorted octahedron, of which the equatorial plane is formed by four amino N atoms of two *trans*-oriented cyclohexane-1,2-diamine ligands (Table 1). The axial positions in the octahedron are occupied by two N atoms of two accesulfamate ligands with the Cu–N distance being longer than the corresponding distances in related structures (Tables



Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. (The symmetry code is as in Table 2.)



Figure 2

A view of the molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. (The symmetry code is as in Table 4.)

1 and 6). This elongation can be attributed to the static Jahn– Teller effect (Jahn & Teller, 1937) discussed below. Ring puckering parameters (Cremer & Pople, 1975) for (I) and (II) are given in Table 5. Atoms N1 and N2 are bonded to Cu1 to form a five-membered chelate ring (C1/N1/Cu1/N2/C6) while the acesulfame ring adopts a half-chair conformation and the cyclohexane C1–C6 ring adopts a chair conformation. The Cu–N bond lengths (Tables 1 and 6) are very similar to those reported by Pariya, Liao *et al.* (1998).

Compound (II) consists of Zn^{II} ions bonded by two mutually *trans* cyclohexane-1,2-diamine ligands and two aqua ligands, two acesulfamate anions and two water molecules (Fig. 2). The Zn^{II} ion is located on a symmetry centre and has the overall geometry of a slightly tetragonally distorted octahedron, with the equatorial plane formed by four N atoms of



Figure 3

Part of the crystal structure of (I), showing the formation of $R_2^2(12)$ rings. H atoms not involved in these interactions have been omitted for clarity. (The symmetry codes are as in Table 2.)



Part of the crystal structure of (I), showing the formation of an edge-fused chain of $R_2^2(12)$ rings. H atoms not involved in these interactions have been omitted for clarity. (The symmetry codes are as in Table 2.)

two cyclohexane-1,2-diamine groups (Table 3). The axial positions in the octahedron are occupied by two aqua O atoms. Atoms N1 and N2 are bonded to Zn1 to form a fivemembered chelate ring (C1/N1/Zn1/N2/C6) with the acesulfame anion ring adopting a similar half-chair conformation to the bound ligand in (I) (Table 5). The cyclohexane C1-C6 ring also adopts a similar chair conformation. The Zn-N bond lengths are very similar to those reported by Lalehzari et al. (2008). In each compound, the S=O and C=O distances are in good agreement with those found for structures containing the acesulfame ring [see, for example, İçbudak, Bulut et al. (2005) and Dege et al. (2007)]. The slight difference between the carbonyl bond distances of both complexes can be explained in terms of different hydrogen-bond involvement of this group. That is, in the Cu complex, (I), the carbonyl group only interacts with the amino group of cyclohexane-1,2diamine, while this group further interacts with an aqua ligand and water molecule in the Zn complex.



Figure 5

Part of the crystal structure of (II), showing the formation of an edgefused chain of $R_2^1(6)$, $R_3^3(13)$ and $R_4^4(16)$ rings. H atoms not involved in these interactions have been omitted for clarity. (The symmetry codes are as in Table 4.)



Part of the crystal structure of (II), showing the formation of $R_2^1(6)$ and $R_3^2(8)$ rings. H atoms not involved in these interactions have been omitted for clarity. (The symmetry codes are as in Table 4.)

Both octahedral complexes in (I) and (II) exhibit tetragonal distortion by elongation along the axial (z) direction (Table 6). The tetragonal distortion in (I) is attributed to the nonspherically symmetric electronic configuration (Jahn-Teller effect) of $Cu^{2+}(d^9)$ (Pariya, Panneerselvan *et al.*, 1998), and the difference between ligands in equatorial (transcvclohexane-1,2-diamine) and axial positions (acesulfamate). In (II), the smaller tetragonal distortion corresponds to the difference between the ligands in the equatorial (trans-cyclohexane-1,2-diamine) and axial positions (aqua) given the symmetrical state of the Zn^{2+} (d^{10}) ion and the different overall charge (2+) of the complex cation. Comparisons of M-N distances ($M = Cu^{II}$ and Zn^{II}) in related tetragonally distorted octahedral compounds are given in Table 6. These show that the tetragonal distortion for (I) is at the extreme range of that found in similar compounds.

Molecules are linked by intermolecular hydrogen bonding, and we employ graph-set notation (Bernstein *et al.*, 1995) to describe the resulting patterns. Molecules of (I) are linked into sheets by a combination of $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds (Table 2). Figs. 3 and 4 show the way in which the amino group, carbonyl O atom, sulfonyl O atom and methyl atom C10 enter into intermolecular hydrogen-bonding interactions (symmetry codes are as in Tables 2 and 4). Atom N1 acts as a hydrogen-bond donor, *via* atom H3, to atom O3ⁱ, so forming an S(6) motif. Atom N2 acts as a hydrogen-bond donor, *via* atom H4, to atom O3ⁱⁱ, so forming a centrosymmetric $R_2^2(12)$ ring centred at $(0, \frac{1}{2}, \frac{1}{2})$. Atom C10 acts as a hydrogen-bond donor, *via* atom H10*B*, to atom O1^{iv}, so forming a C(6) motif running parallel to the [$\overline{100}$] direction. The combination of the N-H···O and C-H···O hydrogen bonds produces an $R_2^2(12)$ ring (Fig. 3). The intramolecular N1-H2···O1 hydrogen bond forms an S(6) motif. Atom N2 acts as a hydrogen-bond donor, *via* atom H5, to atom O2ⁱⁱⁱ, so forming C(6) chains running parallel to the [001] direction. The combination of the C(6) chains along [001] generates a chain of edge-fused $R_2^2(12)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n + 1)$ (n = zero or integer) (Fig. 4).

In (II), the two-dimensional assemblies are formed by a combination of N-H···O, O-H···O and C-H···O hydrogen bonds (Table 4). The free water atom (O2) acts as hydrogen-bond donor, *via* atoms H3 and H4, respectively, to atoms O5^{iv} and O3ⁱⁱ, so forming a centrosymmetric $R_4^4(16)$ ring centred at $(\frac{1}{2}, 1, \frac{1}{2})$. The combination of the N2-H9···O2, $C6^i$ -H6ⁱ···O4^{iv}, O2-H3···O5^{iv} and O2-H4···O3ⁱⁱ hydrogen bonds along [110] generates a chain of edge-fused $R_3^3(13)$ and $R_4^4(16)$ rings. In addition to these, C6-H6···O4ⁱⁱⁱ and C2-H2A···O4ⁱⁱⁱ hydrogen bonds produce an $R_2^1(6)$ ring (Fig. 5). Similarly, the combination of the N2-H8···O5, N1-H11···O2ⁱⁱⁱ and O1-H2···O5ⁱ hydrogen bonds produces $R_2^1(6)$ and $R_3^2(8)$ rings (Fig. 6).

Whether (I) and (II) exhibit (thermo)chromotropic properties will be part of our continuing studies, in the light of these structural and crystal-packing results.

Experimental

[Cu(acs)₂(H₂O)₄] and [Zn(acs)₂(H₂O)₄] were synthesized as reported by İçbudak *et al.* (2006). A solution of (\pm) -*trans*-cyclohexane-1,2diamine (2 mmol) in ethanol (50 ml) was added dropwise with stirring to a 343 K solution of [Cu(acs)₂(H₂O)₄] (1 mmol) in ethanol (50 ml). The solution was stirred at 343 K for 2 h and then cooled to ambient temperature. The resulting blue crystals of (I) were washed with an acetone-1,2-dichloroethane (1:1 ν/ν) mixture and dried under vacuum (yield 85%). Elemental analyses: found (calculated) for C₂₀H₃₆CuN₆O₈S₂: C 36.87 (38.99), H 6.15 (5.84), N 12.91% (13.64%). Similarly, a mixture of the (\pm) -*trans*-cyclohexane-1,2-diamine (2 mmol) and [Zn(acs)₂(H₂O)₄] (1 mmol) yielded (II) as colourless crystals (yield 88%). Elemental analyses: found (calculated) for C₂₀H₄₄N₆O₁₂S₂Zn: C 36.77 (34.81), H 6.13 (6.38), N 12.87% (12.18%).

Compound (I)

Crystal data	
$[Cu(C_4H_4NO_4S)_2(C_6H_{14}N_2)_2]$	V = 1419.30 (8) Å ³
$M_r = 616.21$	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.3878 (2) Å	$\mu = 0.97 \text{ mm}^{-1}$
b = 22.2436 (9) Å	T = 296 K
c = 8.6550 (3) Å	$0.47 \times 0.44 \times 0.33 \text{ mm}$
$\beta = 93.716 \ (2)^{\circ}$	

Data collection

Stoe IPDS 2 diffractometer	13462 measured reflections
Absorption correction: integration	3391 independent reflections
(X-RED32; Stoe & Cie, 2002)	2964 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.626, \ T_{\max} = 0.748$	$R_{\rm int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of
$wR(F^2) = 0.108$	independent and constrained
S = 1.06	refinement
3391 reflections	$\Delta \rho_{\rm max} = 0.47 \ {\rm e} \ {\rm \AA}^{-3}$
194 parameters	$\Delta \rho_{\rm min} = -0.54 \text{ e} \text{ Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

C7-O3	1.239 (3)	N3-Cu1	2.7175 (16)
N1-Cu1	2.0077 (17)	O1-S1	1.4235 (16)
N2-Cu1	2.0036 (18)	O2-S1	1.4171 (17)
O2-S1-O1	116.47 (11)	N2 ⁱ -Cu1-N3	93.06 (7)
N2-Cu1-N1	84.52 (7)	N1-Cu1-N3	93.67 (7)
N2 ⁱ -Cu1-N1	95.48 (8)	N1 ⁱ -Cu1-N3	86.33 (7)
N2-Cu1-N3	86.94 (7)		

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-\mathrm{H}\cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdots A$
$N1 - H2 \cdots O1$ $N2 - H4 \cdots O3^{ii}$	0.81(3) 0.93(3)	2.25(3) 2.12(3)	2.984 (3) 2.981 (2)	151 (3) 153 (2)
$N1-H3\cdots O3^{i}$ $N2-H5\cdots O2^{iii}$	0.86(3) 0.82(3)	2.07(3) 2.20(3)	2.866(3) 2.997(2)	155(2) 154(3) 164(3)
$C10-H10B\cdots O1^{iv}$	0.96	2.54	3.421 (4)	152

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) -x, -y + 1, -z + 1; (iii) x, y, z + 1; (iv) x - 1, y, z.

Compound (II)

Crystal data

$[Zn(C_6H_{14}N_2)_2(H_2O)_2](C_4H_4-$	$\beta = 80.522$ (9)
$NO_4S)_2 \cdot 2H_2O$	$\gamma = 77.176$ (9
$M_r = 690.10$	V = 755.56 (
Triclinic, P1	Z = 1
a = 6.7489 (8) Å	Mo Kα radia
b = 8.8871 (11) Å	$\mu = 1.02 \text{ mm}$
c = 13.5562 (15) Å	T = 296 K
$\alpha = 73.476 \ (9)^{\circ}$	0.44×0.38

Data collection

Stoe IPDS 2 diffractometer Absorption correction: integration (X-RED32; Stoe & Cie, 2002) $T_{\rm min}=0.646,\ T_{\rm max}=0.795$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.089$ S = 1.032971 reflections 228 parameters 7 restraints

9)° 9)́° 15) Å³ tion × 0.25 mm

7159 measured reflections 2971 independent reflections 2618 reflections with $I > 2\sigma(I)$ $R_{\rm int}=0.023$

H atoms treated by a mixture of independent and constrained refinement $\Delta \rho_{\rm max} = 0.56 \ {\rm e} \ {\rm \AA}^{-3}$ $\Delta \rho_{\rm min} = -0.36 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

C7-O5	1.251 (3)	O1-Zn1	2.2631 (19)
N1-Zn1	2.118 (2)	O3-S1	1.4259 (19)
N2-Zn1	2.1270 (19)	O4-S1	1.4201 (18)
O4-S1-O3	116.33 (12)	N2-Zn1-O1	89.50 (8)
N1-Zn1-N2	81.81 (7)	$N1-Zn1-O1^{i}$	89.73 (9)
N1-Zn1-O1	90.27 (9)	$N2-Zn1-O1^{i}$	90.50 (8)

Symmetry code: (i) -x + 2, -y + 1, -z + 1.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
N2−H8···O5	0.85 (3)	2.60 (3)	3.324 (3)	143 (2)
$N2-H9\cdots O2$	0.84 (3)	2.21 (3)	3.042 (3)	170 (3)
$O2-H4\cdots O3^{ii}$	0.81(2)	2.10(2)	2.903 (3)	170 (3)
C6−H6···O4 ⁱⁱⁱ	1.10 (3)	2.55 (3)	3.530 (3)	147.5 (19)
$C2-H2A\cdots O4^{iii}$	0.97	2.58	3.430 (3)	147
$N1 - H11 \cdots O2^{iii}$	0.84(3)	2.30 (3)	3.108 (4)	163 (2)
$O2-H3\cdots O5^{iv}$	0.82(2)	1.89 (2)	2.698 (3)	169 (4)
$O1\!-\!H2\!\cdots\!O5^i$	0.81 (2)	2.03 (2)	2.818 (3)	163 (3)

Symmetry codes: (i) -x + 2, -y + 1, -z + 1; (ii) x, y + 1, z; (iii) x + 1, y, z; (iv) -x + 1, -y + 1, -z + 1.

Table 5

Puckering parameters (Å, °) (Cremer & Pople, 1975).

Ring	Q	θ	φ
(I) \$1/O4/C9/C8/C7/N3	0.4395 (16)	60.7 (3)	11.4 (3)
(II) S1/O6/C9/C8/C7/N3	0.3781 (16)	62.4 (3)	5.7 (4)
(I) C1–C6	0.529 (4)	178.2 (4)	104 (12)
(II) C1–C6	0.563 (3)	3.6 (3)	181 (5)

For (I), 16 reflections affected by the backstop or clearly outlier data were omitted from the refinement using OMIT (SHELXL97; Sheldrick, 2008). For both structures, the water H atoms were located in a difference map and refined subject to a DFIX (SHELXL97; Sheldrick, 2008) restraint of O-H = 0.83 (2) Å. The H atoms bonded to amino N atoms (N1 and N2) and C atoms (C1 and C6) were located in a difference map and refined freely. The methyl H atoms were constrained to an ideal geometry (C-H = 0.96 Å), with $U_{iso}(H)$ = $1.5U_{eq}(C)$, but were allowed to rotate freely about the adjacent C-C bonds. The other H atoms attached to C atoms were refined using a riding model, with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic C atoms, and C-H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene C atoms, since they could not be located from the Fourier map.

For both compounds, data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA; data reduction: X-RED (Stoe & Cie, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3156). Services for accessing these data are described at the back of the journal.

Table 6

Comparison of Zn,Cu-N bond distances (Å) and angles (°) in related compounds.

Compound	(Cu,Zn)-N (equatorial)	(Cu,Zn)-O,N axial	N $-M$ $-$ N angle most distorted from 90°	Reference
(I)	2.077 (17), 2.0036 (18)	2.7175 (16)	95.48 (8)	This paper
(II)	2.118 (2), 2.1270 (19)	2.2631 (19)	90.50 (8)	This paper
$[Cu(dmen)_2(H_2O)_2](acs)_2^{\dagger}$	2.035 (2), 2.051 (2)	2.479 (2)	94.9 (1)	İçbudak, Uyanık et al. (2007)
6-Cu(II)OTf‡	2.019 (7), 2.017 (6), 2.056 (4), 2.022 (5)	2.530 (4), 2.525 (4)	85.3 (2)	Fonseca et al. (2003)
[Cu(dmen) ₂ (H ₂ O) ₂](sac) ₂ †§	2.040 (2), 2.052 (2)	2.522 (2)	94.7 (1)	İçbudak et al. (2003)
$[Cu(dpyam)_2(H_2O)_2](S_4O_6)$	2.001 (2),2.021 (2)	2.458 (3)	94.05 (8)	Youngme & Chaichit (2005)
[Cu(dpyam) ₂ (CF ₃ SO ₃) ₂]	1.983 (7), 1.999 (7), 2.022 (7), 2.030 (7)	2.498 (7), 2.471 (7)	95.2 (3)	Youngme & Chaichit (2002)
$[CuL_2(H_2O)_2]Cl_2^{\dagger\dagger}$	2.044 (2), 2.027 (3)	2.590 (2)	95.8 (1)	Pariya, Liao et al. (1998)
$[CuL_2(NO_3)_2]^{\dagger\dagger}$	1.990 (4), 2.006 (4)	2.620 (3)	95.2 (2)	Pariya, Liao et al. (1998)

 \dagger dmen is *N,N'*-dimethylethylenediamine. $\ddagger 6$ is *N,N'*-bis(2-ethylphenylamino)cyclohexane and OTf is trifluoromethanesulfonate. § sac is 1,1-dioxo-1,2-benzothiazol-3-one. ¶ dpyam is di-2-pyridylamine. \dagger *t* is cyclohexane-1,2-diamine.

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